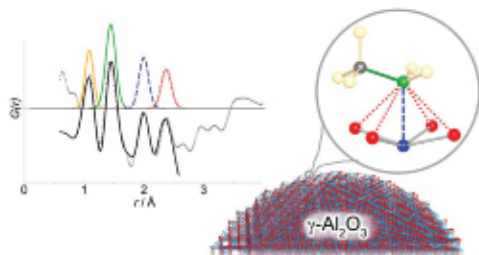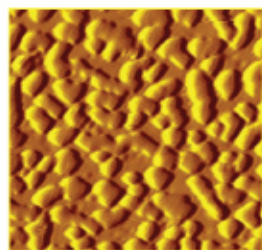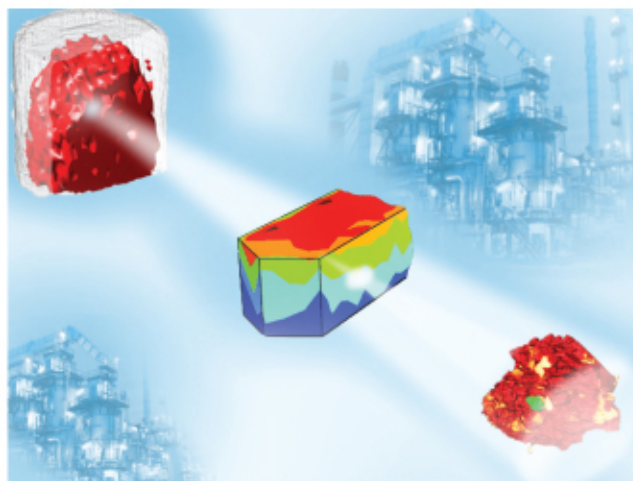# *In-situ* Characterization of Heterogeneous Catalysts

Edited by
José A. Rodriguez, Jonathan C. Hanson,
and Peter J. Chupas

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IN-SITU CHARACTERIZATION OF HETEROGENEOUS CATALYSTS

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INTRODUCTION: GOALS AND CHALLENGES FOR THE *IN-SITU* CHARACTERIZATION OF HETEROGENEOUS CATALYSTS

José A. Rodriguez, Jonathan C. Hanson, and Peter J. Chupas

CATALYSIS AND THE NEED TO CHARACTERIZE ACTIVE SITES IN DIFFERENT TYPES OF MATERIALS AND CHEMICAL ENVIRONMENTS

Catalysis is central to the production of fuels and chemicals, including more than 70% of today's chemical products. About 20% of the value of all commercial products manufactured in the United States is derived from processes involving catalysis [1–3]. Thus, the understanding and optimization of heterogeneous catalysts is a critical need within the chemical industry [2, 3]. The most important considerations when designing a new catalyst or when optimizing the performance of an existing one are activity, selectivity, and durability [3]. The catalyst must be able to perform a reaction of interest at an acceptable rate under a practical set of temperatures and pressures. There is a commercial incentive to tune catalysts to operate at low temperatures and pressures [2, 3]. It is concurrently important that the rate of side reactions be minimal, and the catalyst must be able to sustain the desired reaction over long periods of time [3]. When designing or optimizing a catalyst, one must know the nature of its active sites and how they interact with the reactants, intermediates, and products of a catalytic process. The structural and electronic properties of the active

sites are usually affected by the chemical environment in which they operate. This book describes experimental techniques that have been developed to characterize catalysts and study reaction mechanisms *in situ* under academic and technical or industrial conditions.

Heterogeneous catalysts can be metals, oxides, carbides, sulfides, nitrides, practically any type of material [1–3]. In the nineteenth century it was already known that all the regions or atoms in the surface of a heterogeneous catalyst are not involved in the real catalytic process. The concept of the "active site" in catalysis has been used since its introduction in the 1920s by Taylor and Langmuir [4, 5]. However, despite considerable scientific effort over many years, our knowledge of what exactly the active sites are and how they really work is in most cases very primitive [6]. First, it is necessary to identify the active site and fully characterize its electronic and structural properties under reaction conditions. Since industrial catalysts and catalytic processes are extremely complex [2, 3], the development of techniques for the characterization of catalytic systems *in situ* as they evolve in time with a changing chemical environment is a very challenging task. Figure I.1 shows four different types of systems which are frequently used in catalytic studies. Figure I.1A displays an image of high-resolution transmission electron microscopy (HR-TEM) for a high surface area Pt-Ru/CeO_2 catalyst [7]. One sees particles of a Pt–Ru alloy (1.5–3 nm in size) on top of a ceria support that mainly exhibits the (111) face of the oxide. In the case of Figure I.1B, the HR-TEM image corresponds to a Pt/CeO_x/TiO_2 catalyst [8]. The loading of Pt is very low (0.5 wt%) and the small particles of the metal (0.4–0.5 nm) are difficult to detect with HR-TEM. The TiO_2 support nanoparticles are monocrystalline and present an average size of 10–15 nm. The bright spots as indicated by the arrows represent CeO_2 nanoparticles with an average diameter of about 4–5 nm. In the Pt/CeO_x/TiO_2 catalyst, the very low content of Pt points to the need for characterization techniques with a high sensitivity. Many catalytic processes are carried out on the type of metal/oxide powder catalyst shown in Figure I.1A,B, with the surface exhibiting a high degree of structural heterogeneity [1–3]. In contrast, when studying correlations between surface "structure" and reactivity, it may be advantageous to do experiments on well-defined single-crystal surfaces such as those displayed in Figure I.1C,D [9, 10]. Furthermore, the system in Figure I.1A has the typical metal/oxide configuration seen in many industrial catalysts [1–3]. However, to enhance the participation of ceria in catalytic reactions, one may adopt an inverse configuration in which nanoparticles of this oxide are deposited on top of the surface of a metal or another oxide [11]. Thus, the inverse CeO_2/CuO and CeO_2/CuO_x/Cu(111) catalysts shown in Figure I.2 exhibit a very high activity for the low-temperature oxidation of CO and the CO preferential oxidation (PROX) reactions [12, 13]. In practical terms, one needs to develop techniques for the *in-situ* characterization of all the systems shown in Figure I.1 and Figure I.2, and even much more complex materials in which there are multiple phases coexisting in a three-dimensional space [14]. When focusing on spatial resolution, characteristic length scales

(A) HR-TEM of Pt-Ru/CeO$_2$

(B) HR-TEM of Pt/CeO$_x$/TiO$_2$

(C) p(2x2)-Sn/Pt(111) surface

(D) TiO$_2$(110), side view
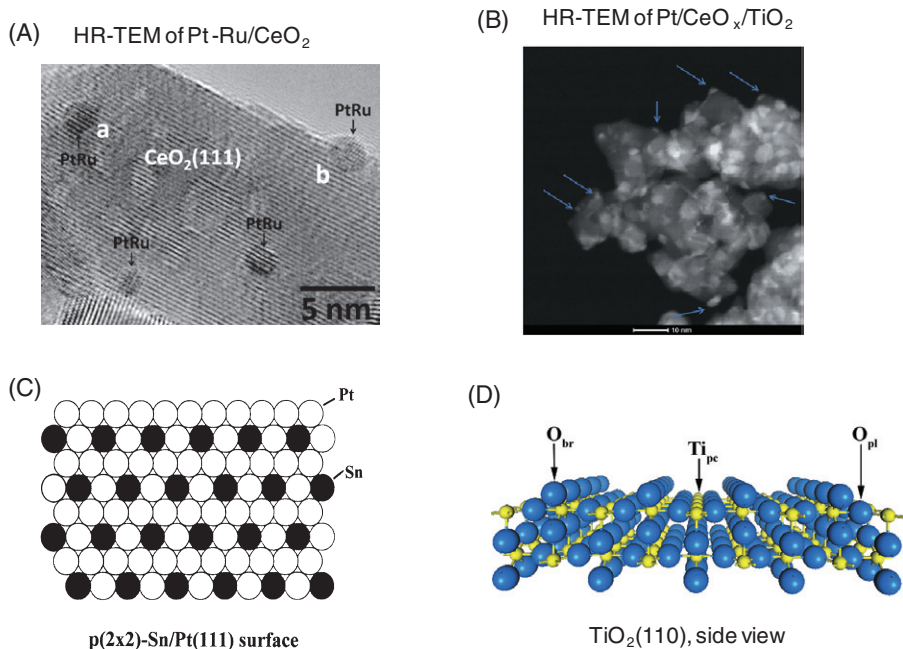
Figure I.1. Different types of systems investigated in studies in the area of catalysis. (A) Image of HR-TEM for a Pt–Ru/CeO2 catalyst. Reprinted with permission from Reference 7. Copyright (2012) Elsevier. (B) Image of HR-TEM for a Pt/CeO$_x$/TiO$_2$ catalyst. Reprinted with permission from Reference 8. Copyright (2012) American Chemical Society. (C) Top view of a Sn–Pt(111) model catalyst. (D) Side view of a TiO$_2$(110) surface.

relevant for catalytic materials range from a few millimeters (usual sample size) to nanometers (typical size of catalytic nanoparticles). If one is interested in the geometrical structure of molecules adsorbed on the surface of the catalyst as reactants or intermediates, then the significant length scale is in the order of angstroms or picometers.

Time is a very important parameter when studying a catalytic process. A phenomenological rate law gives the disappearance of reactants or appearance of products as a function of time for a particular set of reaction conditions (pressure, temperature, and chemical concentrations) [6]. At a microscopic level, molecules are transformed and the chemical environment around the active sites of a catalyst changes as a function of time [6, 10]. In order to obtain a full understanding of the key transformations associated with a catalytic process, one must be able to track the time evolution of the structural and electronic properties of the active site. The activation and breaking of a chemical bond inside a molecule occurs in the picosecond regime but the completion
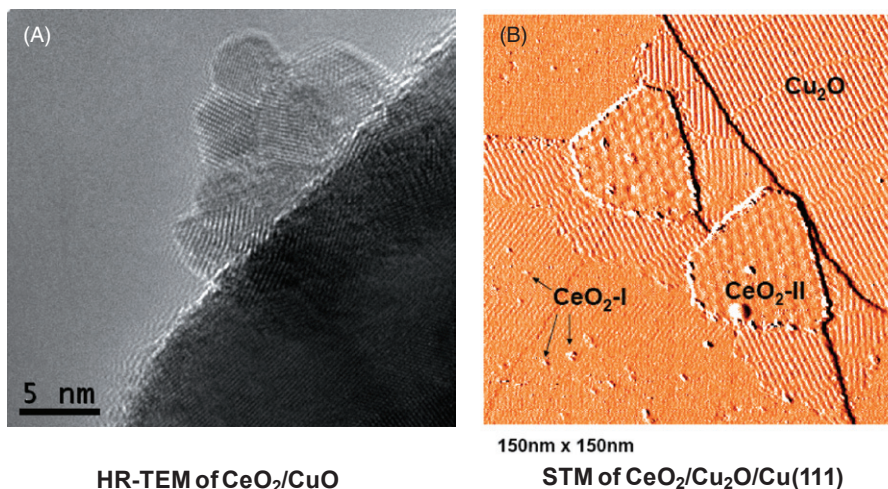
Figure I.2. Inverse ceria/copper oxide catalysts. (A) Image of HR-TEM for a CeO_2/CuO powder catalyst. Reprinted with permission from Reference 12. Copyright (2010) American Chemical Society. (B) Image of STM for a $CeO_2/CuO_x/Cu(111)$ model catalyst. Reprinted with permission from Reference 13. Copyright (2011) American Chemical Society.

of a full reaction cycle on the surface of a catalyst usually takes longer times. Based on turnover rates for typical reactions (10^{-2}–10^3 molecules/site•second) [9, 10], one can estimate that the timescale for a catalytic transformation on the surface of a catalyst is usually in the range of minutes to milliseconds under typical reaction conditions. Ideally, one must be able to track transformations of the catalytic material in this time range. Very valuable information about catalytic processes can be obtained under steady-state conditions (i.e., no variations in temperature, pressure, and reaction rate), but to obtain a detailed understanding of reaction mechanism one frequently has to do experiments in a non-steady-state or transient mode in which the properties of the catalytic system are perturbed by changing the temperature (see Fig. I.3), or by pulses (fluctuations) in the pressures of the reactants [5, 6, 15]. In principle, the perturbations in the reaction conditions can affect the structural properties of the catalyst (Fig. I.3 and Fig. I.4) and the lifetime of surface intermediates that are produced during the reaction.

On the basis of the considerations discussed in the previous paragraphs, one finds that the ideal tool for a detailed study of typical catalytic processes should have high sensitivity and allow us the fast acquisition of data in a milliseconds timescale with a spatial resolution in the range of nanometers or smaller, monitoring simultaneously the properties of the catalyst active sites and the adsorbed reaction intermediates. This is a highly demanding set of requirements. At the present time, no single technique can accomplish all of these tasks. For a complete characterization of a catalytic process, one must
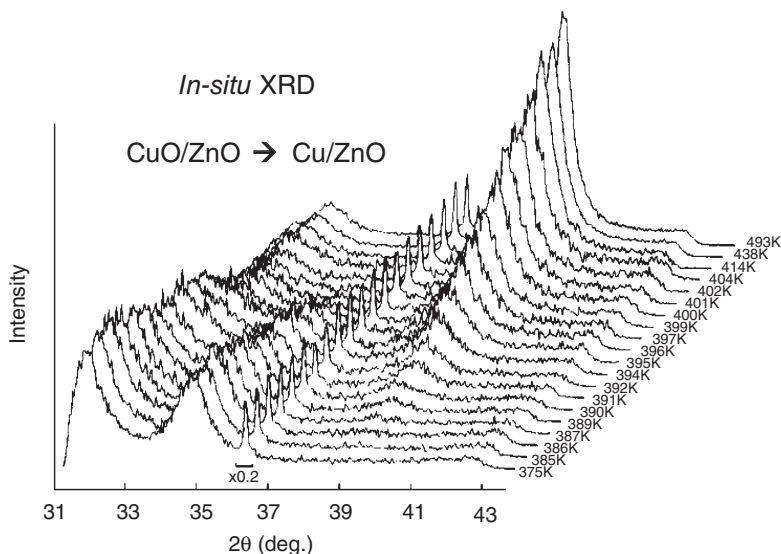
Figure I.3. Three-dimensional plot of *in-situ* XRD patterns collected during the reduction/activation of a powder CuO/ZnO catalyst in a mixture of 0.25% CO, 0.25% CO$_2$, and 4% H$_2$ in argon. The XRD patterns were collected at temperatures between 375 and 493 K. A CuO $\rightarrow$ Cu structural transformation was seen around 400 K. Reprinted with permission from Reference 5. Copyright (1991) Elsevier.
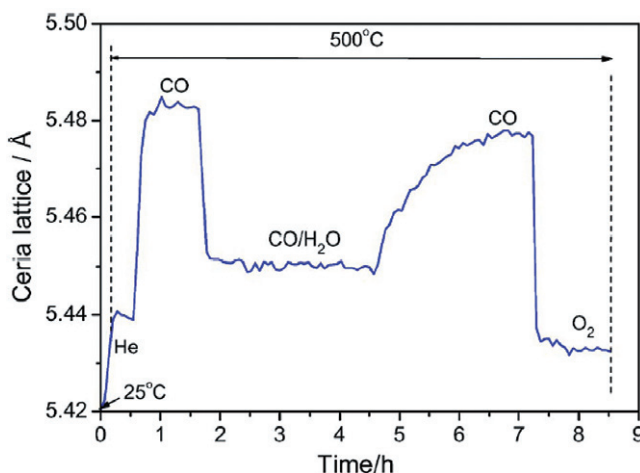
Figure I.4. Variation of the lattice constant of ceria after exposing a powder Au–CeO$_2$ catalyst to CO, the reaction mixture for the water–gas shift reaction (CO/H$_2$O), CO, and O$_2$. The reported values were obtained after analyzing results of time-resolved XRD by Rietveld refinement. Reprinted with permission from Reference 15. Copyright (2006) American Chemical Society.

combine different techniques. Many of the existing techniques focus only on examining the properties of the catalyst, while others are better suited for studying the surface chemistry associated with the reaction process. In practical terms, it is necessary to find a reasonable balance between temporal and spatial resolutions. Techniques which can provide morphological information at the nanometer or subnanometer range do not have the time resolution required for most transient or kinetic studies. Most characterization techniques give average properties for relative large areas (from micrometers to millimeters) of the catalyst sample, making emphasis on obtaining high sensitivity for dealing with low concentrations of elements and for allowing the fast data acquisition necessary for transient experiments.

Nowadays surface science offers a quite impressive array of experimental techniques to investigate the properties of surfaces [6, 10]. Many of these techniques are based on some type of excitation (photons, electrons, neutrons, ions, electromagnetic field, heat, etc.) to which the catalyst responds. A similar type of excitation can be associated with different types of phenomena yielding information about different properties. For example, X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), and X-ray photoelectron spectroscopy (XPS) all use photons for probing the sample and are among the most frequently employed techniques for catalyst characterization [5, 6]. XRD occurs in the elastic scattering of X-ray photons by atoms in a periodic lattice and can be used to obtain structural information. In contrast, irradiating a catalyst with X-ray photons can induce excitation of electrons from occupied core levels to empty valence levels (XAS) or generate photoelectrons (XPS), yielding information about the composition of the sample and the electronic properties of the elements present.

Many surface science techniques operate under vacuum or high-vacuum conditions [6, 10] and cannot be applied in the characterization of catalysts under normal reaction conditions. In order to overcome this problem, several laboratories have developed experimental systems which combine a high-pressure system with an ultra-high-vacuum (UHV) analysis chamber [9, 10, 16]. The high-pressure reactor allows the kinetics of catalytic reactions to be measured on a given surface (see Fig. I.5), while analysis of the structure and composition of the surface both before and after reaction can be accomplished in the UHV chamber. This approach has provided valuable insights into many catalytic processes [9, 10, 16], but it is now clear that the combination of *prenatal* and *postmortem* analysis can miss important changes that occur to the surface of a catalyst under reaction conditions [17–19]. Since surfaces are flexible entities which can reconstruct after interacting with adsorbed molecules (see Fig. I.6 and References [17–19]), one must perform an *in-situ* characterization of the catalyst. In recent years, notable advances in design and instrumentation have added moderate-pressure XPS (Fig. I.7) and high-pressure scanning tunneling microscopy (HP-STM) [17, 20, 21] to the arsenal of techniques that is available for the *in-situ* characterization of catalysts. Furthermore, there has been an extraordinary effort to develop or improve characterization
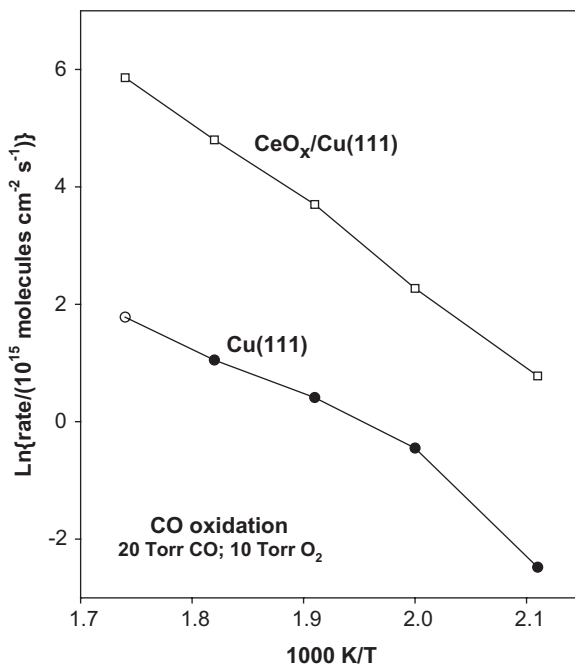
Figure I.5. Arrhenius plots for the $2CO + O_2 \rightarrow 2CO_2$ reaction on Cu(111) and on a surface in which ceria nanoparticles covered ~18% of the copper substrate. $P_{CO} = 20$ Torr, $P_{O_2} = 10$ Torr. Reprinted with permission from Reference 13. Copyright (2011) American Chemical Society.
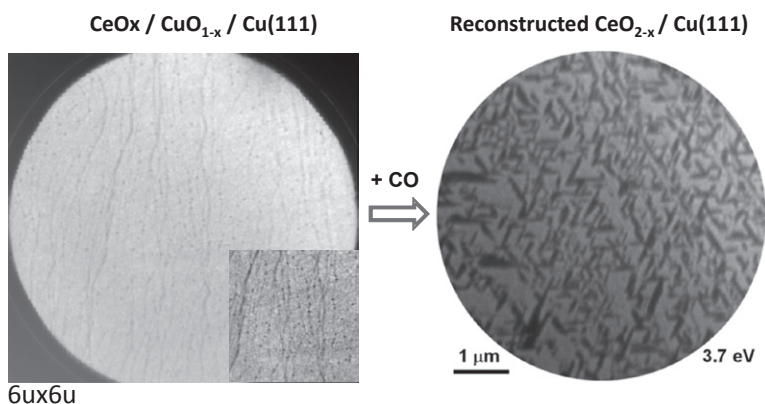
Figure I.6. Images of *in-situ* low-energy electron microscopy obtained before and during the exposure of a $CeO_x/CuO_x/Cu(111)$ model catalyst to CO [19]. In the final step, the system consisted of ceria nanoparticles dispersed on a reconstructed Cu(111) surface. Reprinted with permission from Reference 19. Copyright (2012) American Chemical Society.

$C\ 1s\ \ h\nu = 490\ eV$ $O\ 1s\ \ h\nu = 735\ eV$

$0.1\ torr\ CO_2 + 0.1\ torr\ H_2O$

(B)

289.3
carbonate

285.2
methoxy

531.9
carbonate

531.1
OH

233.0
$H_2O_{(a)}$

287.3
formate

284.4
C^0

Zn/Cu

529.8
ZnO

288.4
$CO_2^{\delta -}$

(A)

531.4
$CO_2^{\delta -}$

530.8
OH

Cu

529.8
$O_{(a)}$

296   292   288   284

540   536   532   528

Binding Energy (eV)

Binding Energy (eV)
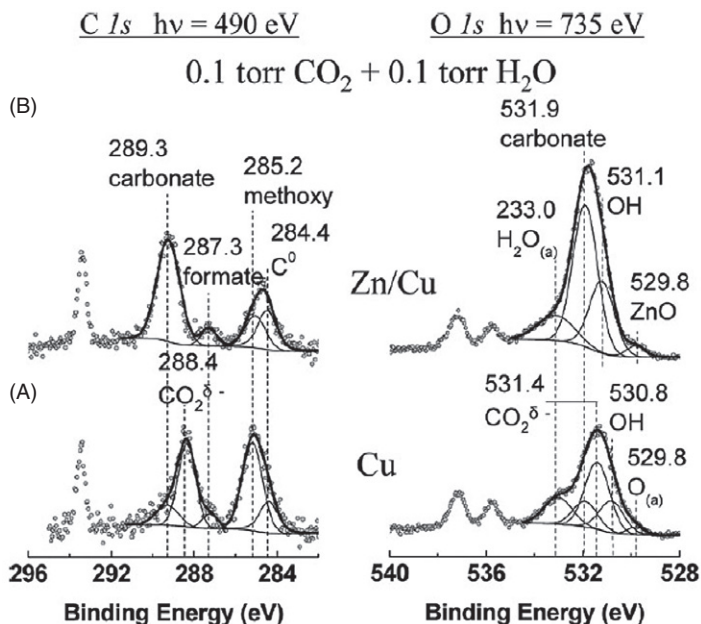
Figure I.7. Carbon and oxygen 1s XPS spectra of (A) pure Cu and (B) Zn/Cu (0.1 mL Zn) in the presence of 0.1 Torr of CO_2 and 0.1 Torr of H_2O at room temperature. Two carbonaceous species, formate and methoxy, are shown to form on both surfaces. Activated CO_2 and carbonate species present in pure CO_2 remain visible on each surface. In addition, molecularly adsorbed H_2O is also observed in both spectra. The presence of Zn makes carbonate the majority species on the surface. Reprinted with permission from Reference 20. Copyright (2009) Elsevier.

techniques which take advantage of synchrotrons or neutron facilities. It is in these facilities where major advances have been made in the development of techniques which allow us the structural characterization of crystalline or amorphous materials [22–26], dealing with diluted samples [26, 27], the fast acquisition of data [27–29], and catalyst imaging [24, 26, 30]. There has also been substantial progress in the integration of techniques for the simultaneous study of the catalyst properties and reaction mechanism [25, 30–34].

This book is divided in 16 chapters which cover recent advances in an array of techniques which can be used to study *in-situ* catalytic processes taking place on high-surface area powders or on well-defined model catalysts. Using these techniques, one can perform fundamental studies of the physical and chemical properties of a catalyst obtaining information about composition, structural features, surface morphology, electronic states, and chemical reactivity. Figure I.8 shows a typical approach followed nowadays in the study of catalytic processes. First, one must identify and characterize the active phase

Integral approach to catalysis:
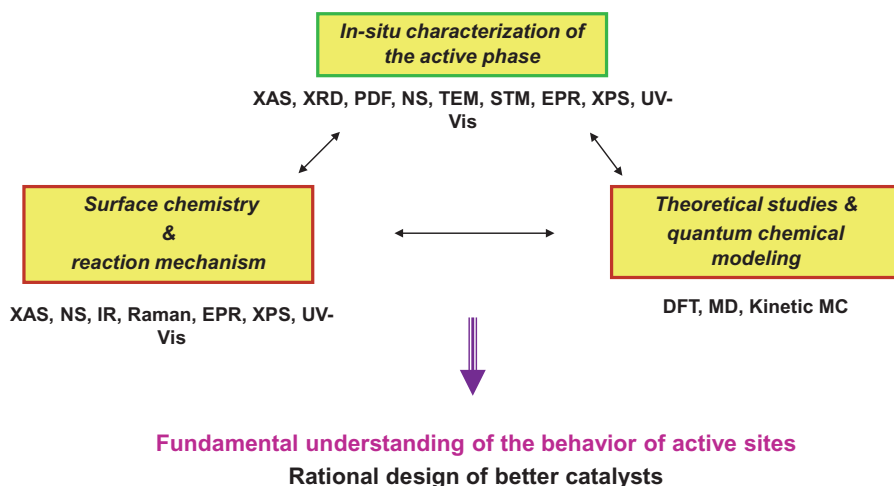
Figure I.8. Different areas of research during the study of catalytic processes. A fundamental understanding is obtained by combining *in-situ* characterization of the active phase in the catalyst with experimental and theoretical studies of the surface chemistry associated with the catalytic process. NS, neutron scattering; TEM, transmission electron microscopy; EPR, electron paramagnetic resonance; UV-Vis, ultraviolet–visible spectroscopy; IR, infrared; DFT, density functional theory; MD; molecular dynamics; MC, Monte Carlo.

of the catalyst. This is usually followed by studies of surface chemistry aimed at obtaining the details of the reaction mechanism. Theoretical studies can provide a conceptual frame for understanding the properties of the catalyst or the steps in the reaction mechanism [35, 36]. The integral approach shown in Figure I.8 eventually can yield a fundamental understanding of the behavior of active sites which can be used for the rational design of better catalysts. This approach usually takes advantage of the *in-situ* techniques described in this book.

CATALYST COMPOSITION AND ACTIVE PHASE IDENTIFICATION

The fist step in any catalytic study is to identify the composition and active phase of the catalyst under reaction conditions. XAS is perhaps the technique most frequently used for this task. The first three chapters in the book show different versions of XAS, making emphasis in time and spatial resolution.

XAS is one of the most powerful techniques available to follow the composition of catalysts as a function of time in kinetic or transient studies [27–29]. It also can be used to study spatial gradients of composition in chemical reactors [24, 26, 30].

XPS is among the most used techniques to measure the composition and chemical state of catalysts *ex situ* under high-vacuum conditions [6]. Chapter 12 describes recent developments in instrumentation [17, 20, 21] which now make possible the use of XPS to determine the composition of catalysts under moderate pressure conditions. XRD is also one of the most frequently applied techniques in catalyst characterization [37]. If the sample has long-range order, then time-resolved XRD is an extremely powerful tool to identify the active phase of a catalyst (see Fig. I.3 [5] and Fig. I.9 [38]) and to follow its behavior as a function of time with changing temperature or pressure (Chapter 4). Depending on the nature of the sample, neutron scattering (Chapter 6), infrared spectroscopy (Chapter 8 and Chapter 9), Raman spectroscopy (Chapter 10, Chapter 15, and Chapter 16), and electron paramagnetic resonance spectroscopy (Chapter 11) also can provide information about the nature of the active phase in a catalyst, although some of these techniques are better suited for studying adsorption and surface reactions.

STRUCTURAL FEATURES AND SPATIAL ARRAY OF THE ACTIVE PHASE IN THE CATALYST

The actual structure of the active phase of a catalyst can range all the way from crystalline to amorphous [1–3]. Furthermore, a part of the catalyst can be crystalline and another amorphous. This is a frequent situation seen in metal/oxide catalysts where the oxide support is mainly crystalline and small metal particles are amorphous (Fig. I.1B). In a common terminology used in the area of crystallography [37], the structure of a catalyst can have local, medium-, or long-range order. This book describes four techniques that can be used to obtain detailed information about the structure of catalysts: extended X-ray absorption fine structure (EXAFS; Chapter 1, Chapter 2, and Chapter 3), X-ray powder diffraction (Chapter 4), pair distribution function (PDF) analysis (Chapter 5), and neutron diffraction (Chapter 6). These techniques respond to different ranges of crystallinity or order in the sample.

X-ray powder diffraction and neutron diffraction require long-range crystalline order. XRD is one of the oldest and most frequently applied techniques for the structural characterization of catalysts [6, 37]. It is frequently used to identify crystalline phases inside catalysts, by means of diffraction lines and the corresponding lattice structural parameters, and to obtain an indication of particle size [6, 37]. Furthermore, time-resolved XRD (Chapter 4) provides a convenient way to study lattice variations in the catalyst structure as a function of temperature and pressure of the reactants (Fig. I.4). A large penetration depth and a high sensitivity to lighter elements, especially mobile species such
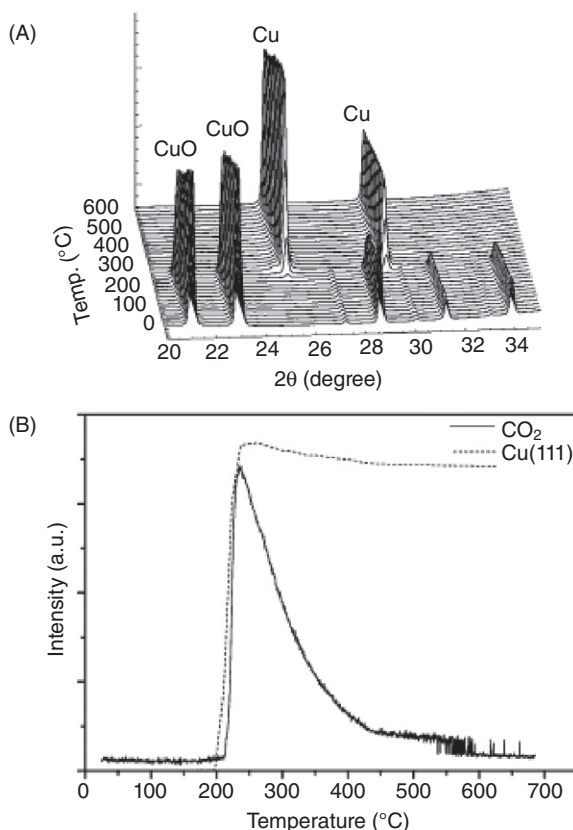
Figure I.9. Temperature-programmed reduction of CuO. (Temperature increase rate = 350°C/h or 5.8°C/min; 5% CO/95% He; gas flow rate ~15–20 mL/min). (A) Time-resolved X-ray diffraction (TR-XRD) patterns. (B) Intensities for the Cu(111) diffraction line in XRD and the CO2 signal (mass-to-charge ratio, m/z) 44 in quadrupole mass spectrometry (QMS) at the exit of the reactor. Reprinted with permission from Reference 38. Copyright (2004) American Chemical Society.

as hydrogen and oxygen, make neutron diffraction an excellent tool to probe heterogeneous catalysts in operational conditions (Chapter 6). Traditionally the use of neutron diffraction in the field of catalysis has been quite limited. However, recent advances in data acquisition and processing together with the availability of higher flux neutron instruments at various facilities now make the study of the structure and dynamics of heterogeneous catalysts using neutrons a realistic goal (Chapter 6).

Traditionally, EXAFS has been the technique of choice for obtaining structural information for samples with a low degree of order (Chapter 1, Chapter

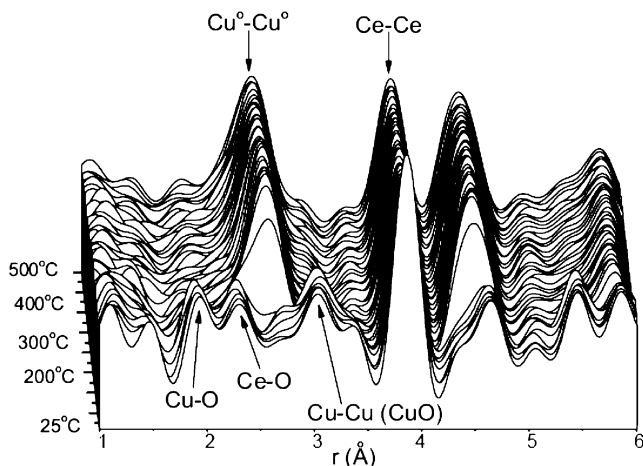**Figure I.10.** Time-resolved PDF analysis of an inverse CeO_2/CuO catalyst under water–gas shift reaction conditions [39]. The CuO initially present in the catalyst is reduced to metallic Cu, whereas the ceria transforms into CeO_{2-x}. Reprinted with permission from Reference 39. Copyright (2010) American Chemical Society.

2, and Chapter 3), but in recent years PDF analysis has emerged as a complimentary technique (Chapter 5). The structural insights within the PDF extend from the local coordination environment, usually measured by EXAFS, up to several nanometers approaching the length scale of particles relevant to most catalytic processes. Since the early 2000s, advances in experimental approach, instrumentation, and detector technologies have increased access to PDF data, providing improved data quality in substantially reduced measurement times (Chapter 5). Nowadays, EXAFS and PDF structural studies can be performed to follow the behavior of catalysts in a wide range of pressures and temperatures (see Fig. I.10) [39]. To measure at the same time the structural parameters of crystalline and amorphous regions of a catalyst sample, one can combine XRD with PDF (Chapter 5) or XRD and EXAFS (Chapter 13). The power of combining XRD and EXAFS is illustrated by a recent study of the reduction of a water–gas shift $CuFe_2O_4$ catalyst in CO [32]. For $CuFe_2O_4$ under reducing conditions, the combined use of the two techniques allowed the acquisition of accurate data for the kinetics of nucleation and growth of metallic Cu (Fig. I.11), the active phase in the catalytic process.

THE SURFACE MORPHOLOGY OF THE CATALYST ACTIVE PHASE

On the basis of studies using well-defined single-crystal surfaces, it is possible to classify catalytic processes into structure-sensitive and structure-insensitive
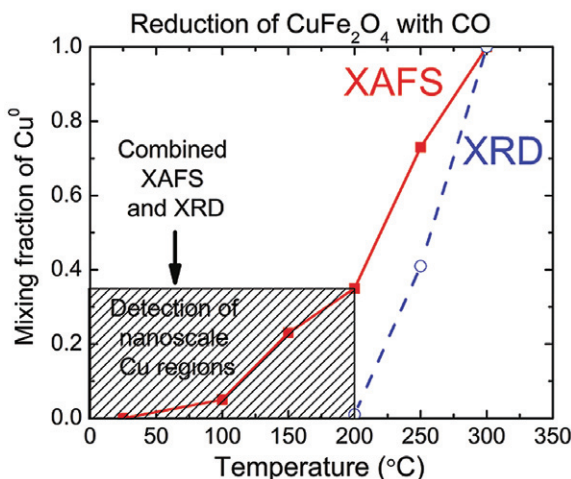
Figure I.11. Comparison of the Cu^0 fractions determined by X-ray diffraction (XRD) and X-ray absorption fine structure (XAFS) for the reduction of a water–gas shift $CuFe_2O_4$ catalysts in CO. Reprinted with permission from Reference 32. Copyright (2011) American Chemical Society.

reactions [9, 10]. If the reaction needs a specific array of sites to turn over, the number of sites may be varied by exposing different crystallographic orientations [6, 9, 10]. In catalysis, a main goal is to induce changes in surface morphology to enhance catalytic activity [10, 18, 36]. This is a very difficult task due to a general lack of knowledge of the behavior of catalytic surfaces under reaction conditions.

Environmental transmission electron microscopy (E-TEM) and HP-STM are two important techniques for studying the surface morphology of powder and model catalysts under reacting gases. Transmission electron microscopy is one the techniques most often used for the *ex-situ* characterization of catalysts [6, 40]. Using this technique the determination of particle size distribution and dispersion is a routine matter. The detection of supported particles is possible if there is sufficient contrast between particles and support (Fig. I.1A). The major limitation of conventional transmission electron microscopy is that it is not an *in-situ* technique [6, 40]. Recent technical developments have made it possible to study the behavior of catalysts under low pressures of a gas [25, 41–43], as shown in Figure I.12. Using aberration-corrected E-TEM, it has been shown that the morphology of an oxide substrate or supported metal particles can depend dramatically on the gaseous environment [25, 42, 43]. Since the 1980s, scanning tunneling microscopy (STM) has been a dominant tool for imaging the surface of single-crystal surfaces (Chapter 7). Studies with STM are usually performed under UHV conditions [10] but, in principle, this
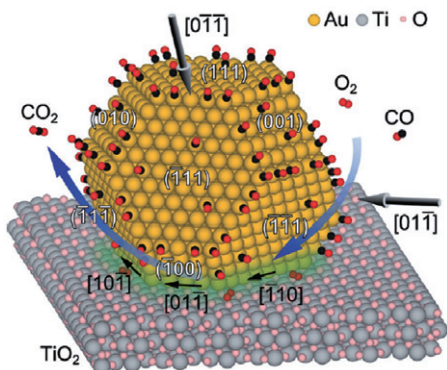
Figure I.12. Instantaneous view of a gold nanoparticle on TiO_2 under reaction conditions (in 1 vol% CO in air [0.75 Torr] at room temperature). The structural model was derived using results of E-TEM. A gold nanoparticle, bounded by {111} and {100} facets, has a polygonal interface with the TiO_2 support. The edges of the polygonal, or perimeter interface, are parallel to the <110> directions. Reprinted with permission from Reference 43. Copyright (2012) John Wiley & Sons.

technique can be applied in a pressure range from UHV to atmospheric or high pressures since the tunneling process between the sample and tip only occurs in a very close range of 3–5 Å. In recent years, remarkable progress has been made in the instrumentation for HP-STM [17, 44]. HP-STM has the unique capability of examining the structure of adsorbates and surface sites of a catalyst *atom by atom* to address several crucial issues of heterogeneous catalysis such as the restructuring of the catalyst surface, the ensemble on surfaces of alloy catalysts, binding site, and even configuration of adsorbates under reaction conditions (Chapter 7).

ELECTRONIC PROPERTIES AND CHEMICAL STATE OF THE ACTIVE PHASE IN THE CATALYST

The reactivity of an atom in a molecule, nanoparticle, or solid is strongly linked to its electronic properties [36, 45]. The identification of the active phase of a catalyst usually involves a determination of the chemical state and electronic properties of the elements present in the system. Over the years several techniques have been developed to probe the core and valence states of solids [6, 46, 47]. XAS (Chapter 1, Chapter 2, and Chapter 3), XPS (Chapter 12), ultraviolet–visible–near infrared spectroscopy (Chapter 16), and electron paramagnetic resonance spectroscopy (Chapter 11) are used widely for probing the electronic properties of atoms in solid catalysts. When acquiring data of XAS and XPS, the high intensity that a synchrotron source provides
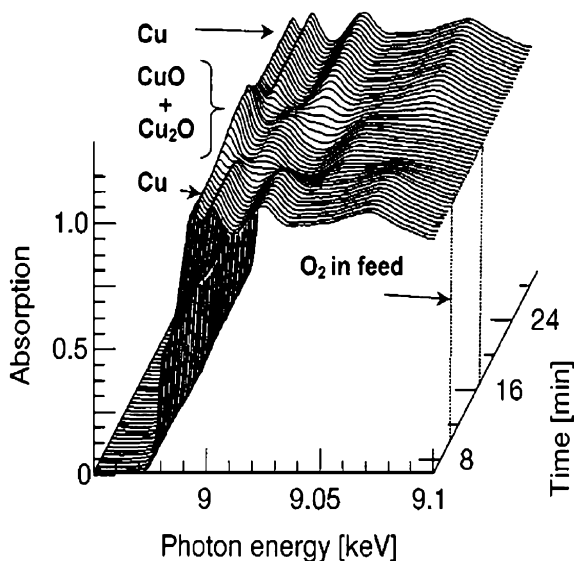
Figure I.13. Evolution of the Cu K-edge XANES of CuO/ZnO at 523 K during oxygen addition to a methanol steam reforming feed (c(MeOH) ~6 vol%, c(H$_2$O) ~1.5 vol% in 25 mL/min He). Different Cu phases are indicated. Reprinted with permission from Reference 48. Copyright (2001) Elsevier.

together with highly efficient detection devices leads to a high-energy resolution that improves our ability to separate different chemical states of an element in a catalyst (see Fig. I.13) [48]. The high intensity of the synchrotron radiation also makes it possible to track fast changes in the electronic properties during transient experiments (Chapter 1, Chapter 3, and Chapter 16) and sample mapping showing spatial gradients of concentration as a function of chemical state (Chapter 2 and Chapter 16). It is known that variations in the geometrical structure of a material usually produce changes in its electronic properties that modify the way in which the material responds to the presence of adsorbates [36]. The integration of instrumentation for XRD and XAS in the same experimental setup (Chapter 13) allows the direct study of possible correlations among the structural, electronic, and catalytic properties of a material.

PROPERTIES OF ADSORBATES, SURFACE CHEMISTRY, AND REACTION MECHANISM

In the scheme of Figure I.8, the determination of the active phase of the catalyst is followed by experimental and theoretical studies on the surface
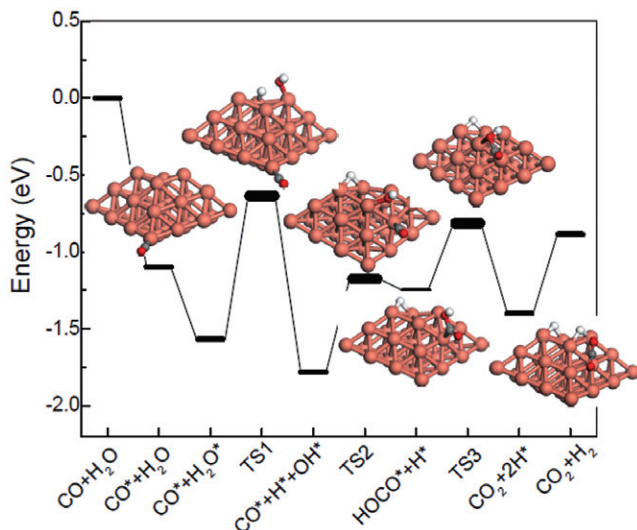
Figure I.14. Calculated energy profile and structures for the water–gas shift reaction $(CO + H_2O \rightarrow H_2 + CO_2)$ on a Cu_{29} nanoparticle [50]. The label "TS" is used to denote a transition state. Reprinted with permission from Reference 50. Copyright (2007) American Institute of Physics.

chemistry and reaction mechanism associated with the catalytic process. The beauty of knowing a reaction mechanism is that it gives us a rational way to improve catalytic activity and selectivity [49]. Figure I.14 shows the calculated energy profile for a possible mechanism of the water–gas shift reaction $(CO + H_2O \rightarrow H_2 + CO_2)$ on a Cu_{29} nanoparticle [50]. The Cu_{29} particle was present in $Cu/CeO_2(111)$ catalysts [51] and the calculations were performed using density functional theory [50]. The interaction of the reactants with Cu_{29} produces significant perturbations in the geometrical structure of the nano-catalyst. Chemical bonds are broken (O–H) and new ones are formed (O–C; H–H). The theoretical study predicts reaction intermediates (OH, H, HOCO) that must be validated by experimental measurements. Ideally, one should be able to monitor simultaneously the changes that occur in the structure of the metal particle and the chemical species that are being transformed on the catalyst surface. Proof of a mechanism for a catalyzed reaction lies in directly observing the chemical species involved in the elementary steps and the kinetics for their transformations [49].

Techniques such as XAS (Chapter 1, Chapter 2, Chapter 3, and Chapter 16), neutron scattering (Chapter 6), infrared spectroscopy (Chapter 8, Chapter 9, and Chapter 16), Raman spectroscopy (Chapter 10 and Chapter 16), electron paramagnetic resonance spectroscopy (Chapter 11), and ambient-pressure

XPS (Chapter 12) can be used to study the adsorption and transformation of chemical species on the surface of a catalyst under reaction conditions. Infrared spectroscopy is perhaps the most commonly used technique in catalysis to identify adsorbed species and to study the way in which these species are chemisorbed in the surface of the catalyst [6]. It is a frequently used technique in mechanistic studies [7, 15, 52–55], having one the longest histories among the methods for *in-situ* characterization [6]. When combined with probe molecules (CO, NO, etc.), infrared spectroscopy can yield valuable information about the adsorption sites in the catalyst [7, 52, 56–58]. Raman spectroscopy has also become popular for *in-situ* studies because it also can give information about the active sites and adsorbed species [52, 59]. Since the selection rules for vibrational transitions in infrared and Raman spectroscopies are different [60], the information obtained from a Raman spectrum often complements that obtained from an infrared study and thus provides valuable structural information (Chapter 10, Chapter 15, and Chapter 16). Inelastic neutron spectroscopy has been used in catalysis research principally due to its high sensitivity to the vibrations of hydrogen atoms (Chapter 6). Hydrogen due to its large incoherent scattering cross section is far more visible by interacting with neutrons than other elements [61], whereas Raman and infrared spectroscopies are more sensitive to the motion of heavier atoms.

Over the years, XPS has proven to be a very useful technique for studying the transformation of molecules on surfaces [10, 46]. The kinetic energy of the photoemitted electron is not only element specific but also contains chemical information because the energy levels of core electrons depend on the chemical state of the atom [46]. With the development of ambient-pressure XPS, it is now possible to study intermediates in common catalytic (Fig. I.7) and electrocatalytic processes (Chapter 12). In many cases, intermediates that are difficult to identify with infrared spectroscopy can be easily identified using XPS and vice versa. Electron paramagnetic resonance spectroscopy is not frequently used in mechanistic studies because it requires paramagnetic species containing unpaired electrons to be present in the system under study [60]. However, when this condition is satisfied, the technique can provide rich information on the local environment of paramagnetic species and how this local environment changes as a reaction progresses (Chapter 11).

The techniques mentioned in the previous two paragraphs, in addition to probe adsorbed species on the surface of a catalyst, can also yield simultaneous information about some properties of the catalytic material during reaction. The last three chapters in the book (Chapter 14, Chapter 15, and Chapter 16) aim at the integration of techniques that provide information on the structural properties of the catalysts, XRD, and X-ray absorption fine structure, with techniques that allow the study of surface reactions: infrared and Raman spectroscopy. A typical example of this type of studies is presented in Figure I.15 [62]. Such integration, a very challenging task, is a significant step forward toward the grand goal of being able to obtain a full picture of all the components in a catalytic process [24, 31, 34, 54, 62].
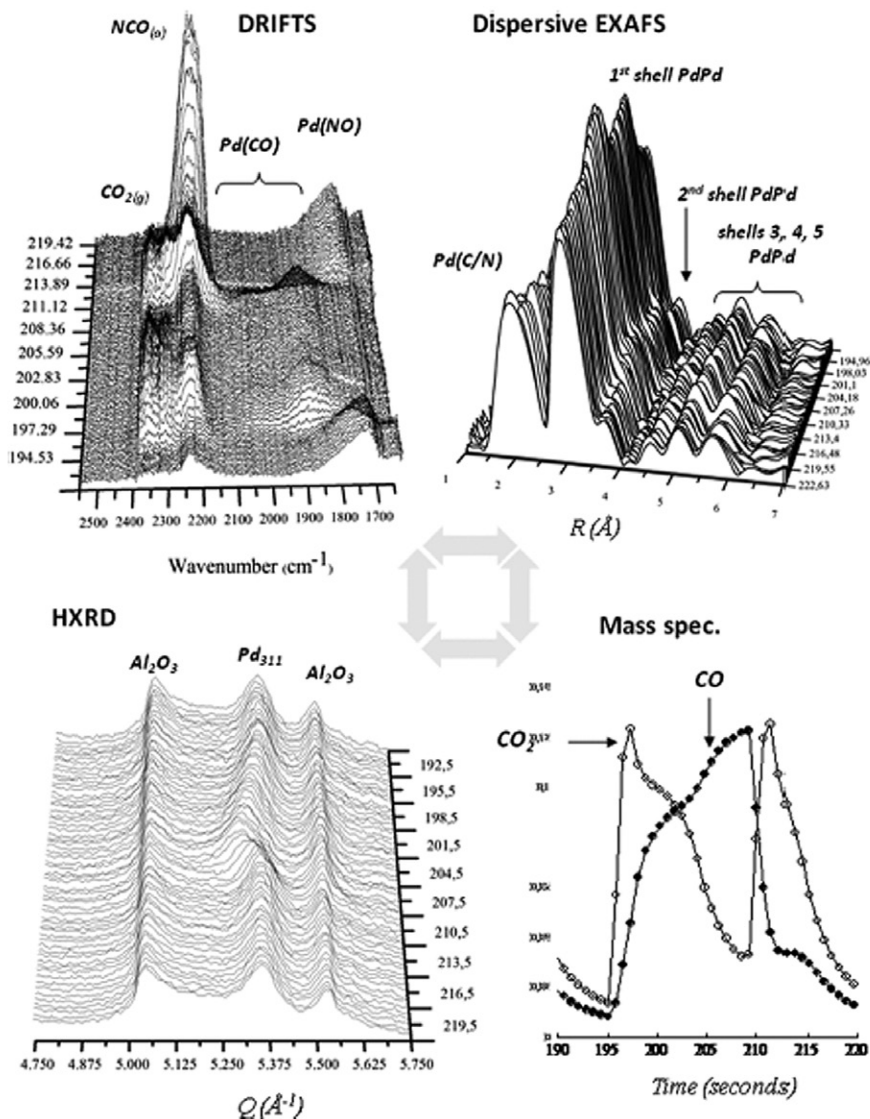
Figure I.15. Multitechnique approach to illuminate CO dissociation and transient carbon storage by Pd/Al_2O_3 during CO/NO cycling. Each of the X-ray techniques may be used in simultaneous time-resolved conjunction with DRIFTS and mass spectrometry (MS). The data from each technique pertain to the structure reactivity behavior of a 2 wt% Pd/Al_2O_3 catalyst during a single switch from 5% CO/He to 5% NO/He at 673 K. Reprinted with permission from Reference 62. Copyright (2010) American Chemical Society.